

APPENDIX - CLAIMS

1. (Currently Amended) A method comprising forming an admixture of a solvent,
an additive, said solvent being different from said additive and
a ~~conjugated diene~~ polymer selected from the group consisting of a precursor to an electrically conductive ~~conjugated diene~~ polymer and an electrically conductive ~~conjugated diene~~ polymer,
said precursor to said an electrically conductive ~~conjugated diene~~ polymer said ~~conjugated diene~~ polymer being made electrically conductive by means of a doping reaction;
said ~~conjugated diene~~ polymer being soluble in said solvent,
said ~~conjugated diene~~ polymer not being substantially soluble in said additive in the absence of said solvent;
said additive provides local mobility to said polymer to allow regions of said ~~conjugated diene~~ polymer to associate with one another to achieve a crystalline state; and
removing or partly removing said solvent, substantially leaving said additive therein as remaining additive, said remaining additive provides local mobility to said ~~conjugated diene~~ polymer to achieve said crystalline state thereby comprising a polycrystalline material, said polycrystalline material is characterized by a degree of crystallinity regions and
a degree of amorphous regions, said degree of crystallinity regions and said degree of amorphous regions are selected by selecting the composition of said additive, and the amount of said additive;
forming a film from said admixture, said film possessing isotropic conductivity.
2. (Canceled) A method according to claim 1, wherein said admixture is electrically conductive and has an isotropic electrical conductivity.
3. (Previously Presented) A method according to claim 1, wherein said additive is selected from the group consisting of plasticizers and diluents.

4. (Currently Amended) A method according to claim 1, wherein said additive is a plasticizer is selected from the group consisting of: Adipic acid plasticizers, Azelaic acid plasticizers, Benzoic acid plasticizers, Citric acid plasticizers, Dimer acid plasticizers, Epoxy plasticizers, Fumaric acid plasticizers, Glycerol plasticizers, Isobutyrate plasticizers, Lauric acid plasticizers, Linoleic acid plasticizers, Maleic acid plasticizers, Sebacic acid plasticizers, Stearic acid plasticizers, Succinic acid plasticizers, Sulfonic acid plasticizers, Terpentines, Terpentine plasticizers, Siloxanes, Polysiloxanes, Ethylene glycols, Polyethylene glycols, Polyesters, Sucrose plasticizers, Mellitates, Myristic acid plasticizers, Oleic acid plasticizers, Palmitic acid plasticizers, Paraffin plasticizers, Phosphoric acid plasticizers, Phthalic acid plasticizers, Ricinoleic acid plasticizers, Tartaric acid plasticizers, Trimellitic acid plasticizers, Glycol plasticizers, Glycolates, Hydrocarbons, Phosphonic acid plasticizers, and Polysilanes.

5. (Previously Presented) A method according to claim 1, wherein said polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylene vinylenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfurans, polypyrroles, polyselenophenes, poly-p-phenylene sulfides, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

6. (Previously Presented) A method according to claim 1, wherein said solvent, when removed or partly removed forms a film which is further stretch oriented.

7. (Currently Amended) A method of fabricating a precursor to an electrically conductive ~~conjugated~~ polymer and an electrically conductive polymer comprising:

admixing a combination of a first material, a second additive doping material and a solvent:

said first material is selected from the group consisting of a precursors to an electrically conductive ~~conjugated~~-diene polymer and an electrically conductive ~~conjugated~~-diene polymer;

said second additive doping material being soluble in said solvent, said second additive doping material not being substantially soluble in said first material in the absence of said solvent;

contacting said first material with said additive doping material to render said first material electrically conductive by means of a doping reaction and providing local mobility to said first material to allow the ~~conjugated~~-diene said polymers to associate with one another to achieve a crystalline state;

removing or partly removing said solvent, substantially leaving said additive doping material therein as a remaining additive doping material, said remaining additive doping material providing local mobility to said first material to achieve said crystalline state thereby comprising a polycrystalline material, said polycrystalline material is characterized by a degree of crystallinity regions and a degree of amorphous regions, said degree of crystallinity regions and said degree of amorphous regions are selected by selecting the composition of said additive, and the amount of said additive;

forming a film from said admixture, said film possessing isotropic conductivity.

8. (Canceled) A method according to claim 7, wherein said combination is electrically conductive and has a conductivity which is isotropic.

9. (Previously presented) A method according to claim 7, wherein said polymer is selected from the group consisting of substituted and unsubstituted polyparaphenylene vinylenes, polythianaphthenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfurans, polypyrroles, polyselenophenes, poly-p-phenylene sulfides, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers and copolymers of the monomers thereof.

10. (Previously presented) A method according to claim 7, wherein said second material is selected from the group consisting of:

Adipic acid plasticizers, Azelaic acid plasticizers, Benzoic acid plasticizers, Citric acid plasticizers, Dimer acid plasticizers, Epoxy plasticizers, Fumaric acid plasticizers, Glycerol plasticizers, Isobutyrate plasticizers, Lauric acid plasticizers, Linoleic acid plasticizers, Maleic acid plasticizers, Sebacic acid plasticizers, Stearic acid plasticizers, Succinic acid plasticizers, Sulfonic acid plasticizers, Terpentines, Terpentine plasticizers, Siloxanes, Polysiloxanes, Ethylene glycols, Polyethylene glycols, Polyesters, Sucrose plasticizers, Mellitates, Myristic acid plasticizers, Oleic acid plasticizers, Palmitic acid plasticizers, Paraffin plasticizers, Phosphoric acid plasticizers, Phthalic acid plasticizers, Ricinoleic acid plasticizers, Tartaric acid plasticizers, Trimellitic acid plasticizers, Glycol plasticizers, Glycolates, Hydrocarbons, Phosphonic acid plasticizers, Polysilanes.

11. (Currently Amended) The method defined in Claim 1 wherein said ~~conjugated~~ polymer is polyaniline crystalline material.

12. (Canceled) A method comprising:
providing solution of polymers in a solvent;
said polymers are selected from the group consisting of precursors to electrically conductive polymers and electrically conductive polymers;
providing mobility to said polymers to allow said polymers to associate with one another to achieve a crystalline state by adding a plasticizer to said solvent;
said plasticizer being soluble in said solvent. said plasticizer not being substantially soluble in said polymer in the absence of said solvent.
13. (Canceled) A method according to claim 12, wherein said step of providing mobility is provided by adding an additive to said solution.
14. (Previously presented) A method according to claim 7 wherein said additive is selected from the group consisting of a plasticizer and a diluent.
15. (Previously Presented) A method according to claim 1, wherein said additive contains substituents which facilitate the miscibility of said polymer and said additive.
16. (Currently Amended) A method according to claim 1, wherein said additive disrupts aggregation of said polymer.
17. - 19 (Canceled)
20. (Previously Presented) A method according to claim 1, wherein said additive deaggregates said polymer.
21. (Canceled)

22. (Previously Presented) A method according to claim 1, wherein said solvent is extracted from said admixture by a technique selected from the group consisting of solvent extraction and evaporation.

23. (Previously Presented) A method according to claim 1, wherein said additive is first added to a solvent and thereafter an electrically conducting polyaniline is added which becomes neutralized upon addition to said admixture.

24. (Previously Presented) A method according to claim 1, wherein said admixture contains a polyaniline, said additive, and an oxidant.

25. (Currently Amended) A method according to Claim 7, wherein said additive includes a plasticization effect.

26 - 39 (Cancelled)

40. (Previously Presented) A method according to claim 7 wherein said additive is an oxidant.

41. (Previously Presented) A method according to claim 7 wherein said material is an oxidant.

42. (Currently Amended) A method according to claim 7 wherein said plasticizer is an oxidant.

43. - 45. (Cancelled)

46. (Canceled) A method comprising forming an admixture of a solvent selected from the group consisting of NMP, m-Cresol and a combination of NMP/m-cresol;
an additive selected from the group consisting of poly-co-dimethyl, amino siloxane, poly glycol diacid, 3,6,9-trioxaundecanoic acid, poly(ethylene glycol) tetrahydrofurfuryl ether, glycerol triacetate, and epoxidized soy bean oil.
polyaniline,
said polyaniline being soluble in said solvent,
said polyaniline not being substantially soluble in said additive in the absence of said solvent;
said additive provides local mobility to said polymer to allow said polymer to associate with one another to achieve a crystalline state; and
removing or partly removing said solvent, substantially leaving said additive therein as remaining additive, said remaining additive provides local mobility to said polyaniline to achieve said crystalline state thereby comprising a polycrystalline material, said polycrystalline material is characterized by a degree of crystallinity regions and
a degree of amorphous regions, said degree of crystallinity regions and said degree of amorphous regions are selected by selecting the composition of said additive, and the amount of said additive,
said admixture being electrically conductive and having an isotropic electrical conductivity.

47. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is epoxidized soy bean oil.

48. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is poly-co-dimethyl, amino siloxane.

49. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is poly glycol diacid.

50. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is 3,6,9-trioxaundecanoic acid.

51. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is poly(ethylene glycol) tetrahydrofurfuryl ether.

52. (Withdrawn) The method according to claim 53, wherein said solvent is NMP and said additive is glycerol triacetate.

53. (Withdrawn) The method defined in Claim 7, comprising forming an admixture of:

a solvent selected from the group consisting of NMP, m-Cresol and a combination of NMP/m-cresol;

an additive selected from the group consisting of poly-co-dimethyl, amino siloxane, poly glycol diacid, 3,6,9-trioxaundecanoic acid, poly(ethylene glycol) tetrahydrofurfuryl ether, glycerol triacetate, and epoxidized soy bean oil.
polyaniline,

said polyaniline being soluble in said solvent,

said polyaniline not being substantially soluble in said additive in the absence of said solvent;

said additive provides local mobility to said polymer to allow said polymer to associate with one another to achieve a crystalline state; and

removing or partly removing said solvent, substantially leaving said additive therein as remaining additive, said remaining additive provides local mobility to said polyaniline to

achieve said crystalline state thereby comprising a polycrystalline material,

said polycrystalline material is characterized by a degree of crystallinity regions and a degree of amorphous regions, said degree of crystallinity regions and said degree of amorphous regions are selected by selecting the composition of said additive, and the amount of said additive.

said admixture being electrically conductive and having an isotropic electrical conductivity.

54. (New) A method comprising forming an admixture of
a solvent selected from the group consisting of DMSO, DMF, NMP, dimethylene propylene urea, tetramethyl urea, pyridine, toluene, m-Cresol, phenol, dimethylacetamide, n-cyclohexylpyrrolidinone, 80% aqueous acetic acid, 60 - 88% aqueous formic acid, pyrrolidinone, N1N' dimethyl propyl urea, benzyl alcohol, and a combination of NMP/m-cresol;
an additive selected from the group consisting of Adipic acid, Azelaic acid, Benzoic acid, Citric acid, Dimer acid, Epoxy, Fumaric acid, Glycerol, Isobutyrate, Lauric acid, Linoleic acid, Maleic acid, Sebacic acid, Stearic acid, Succinic acid, Sulfonic acid, Terpentines, Siloxanes, Polysiloxanes, Ethylene glycols, Polyethylene glycols, Polyesters, Sucrose, Mellitates, Myristic acid, Oleic acid, Palmitic acid, Paraffin, Phosphoric acid, Phthalic acid, Ricinoleic acid, Tartaric acid, Trimellitic acid, Glycol, Glycolates, Hydrocarbons, Phosphonic acid, and Polysilanes,
said solvent being different from said additive and
a polymer selected from the group consisting of a precursor to an electrically conductive polymer and an electrically conductive polymer,
said precursor to said electrically conductive polymer being made electrically conductive by means of a doping reaction with an acid, said polymer being selected from the group consisting of substituted and unsubstituted polyparaphenylene vinylenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfurans, polypyrroles, polyselenophenes, poly-p-phenylene sulfides, polyacetylenes formed from soluble

precursors, combinations thereof and blends thereof with other copolymers of the monomers thereof;

said polymer being soluble in said solvent,

said polymer not being substantially soluble in said additive in the absence of said solvent;

said additive provides local mobility to said polymer to allow regions of said polymer to associate with one another to achieve a crystalline state; and

removing or partly removing said solvent, substantially leaving said additive therein as remaining additive, said remaining additive provides local mobility to said polymer to achieve said crystalline state thereby comprising a polycrystalline material, said polycrystalline material is characterized by a degree of crystallinity regions and a degree of amorphous regions, said degree of crystallinity regions and said degree of amorphous regions are selected by selecting the composition of said additive, and the amount of said additive;

forming a film from said admixture, said film possessing isotropic conductivity.

55. (New) The method defined in Claim 54 wherein said solvent is cresol, said polymer is polyaniline and said additive is poly-co-dimethyl propylamine siloxane.

56. (New) The method defined in Claim 54 wherein said solvent is NMP/cresol, said polymer is polyaniline and said additive is poly-co-dimethyl propylamine siloxane.

Curve Figure 5(a) is a Wide Angle X-Ray Scattering (WAXS) spectrum for a polyaniline base film processed from NMP. The polymer film is essentially amorphous. Curve Figure 5(b) is a Wide Angle X-Ray Scattering spectrum for a polyaniline base film that has been stretch oriented ($1/\lambda = 3.7$). This film was derived from a gel. Curve Figure 5(c) is a Wide Angle X-Ray Scattering spectrum for a polyaniline base film containing 10% of a poly-co-dimethyl propylamine siloxane. This film is highly crystalline.

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Met. 55-57, 753 (1993). WAXS of a stretch oriented film having been stretched ($\lambda/\lambda_0=3.7X$) derived from a gel is shown in Figure 5b. Some crystallinity has been induced as compared to the non-stretch oriented films as evidenced by the defined scattering peaks.

Doping the amorphous polyaniline base films (those having structure shown in Figure 5a) with aqueous hydrochloric acid results in isotropic conductivity of 1 S/cm. Such films are not crystalline. Similar doping of stretch oriented films results in anisotropic conductivity where conductivity on the order of 10^2 S/cm is measured parallel to the stretch direction whereas conductivity on the order of 10^0 S/cm is measured perpendicular to the stretch direction. It should also be noted that some level of crystallinity is lost during the doping process in these films.

According to the present invention, the interchain (polymer chain) registration is increased as compared to a stretch oriented film.

Figures 7 and 8 show the dynamic mechanical thermal analysis (DMTA) spectrum for a polyaniline base film processed from NMP alone. Figure 7 is the first scan where a Tg of approx. 118 is observed as a result of the residual NMP which is present in the film. Figure 8 is the second thermal scan of the same film. This film has no residual solvent and a Tg of ≈ 251 °C is measured for the polyaniline base polymer.

When an additive such as a plasticizer, such as a poly-co-dimethyl propylamine siloxane, is added to the polyaniline base completely different properties and morphology is observed. The siloxane has a polar amine group which facilitates the miscibility of the polyaniline base and the plasticizer. The DMTA of a polyaniline base film cast from NMP and containing 5% by weight to polyaniline of the poly-co-dimethyl propyl amine siloxane exhibits a lower Tg on the

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first thermal scan as compared to polyaniline base processed from NMP alone (Figure 9) as a result of plasticization induced by the siloxane. However, on the second thermal scan of this film (Figure 10), the polymer exhibits an increase in T_g as compared to polyaniline processed from NMP. When the polysiloxane is added to a solution of polyaniline base, the siloxane due to the polar amine group can interact with the polymer chains and disrupt some of the polyaniline interactions with itself or some of the aggregation. Thus, the polysiloxane first induces some deaggregation. However, the polysiloxane has multiple amine sites and thus, it can itself hydrogen bond with multiple polyaniline base chains and thus, the polysiloxane facilitates the formation of a cross-linked network. This cross-linked network accounts for the increased T_g observed in the DMTA. T_g is characteristic of the amorphous regions of a polymer and in this case the amorphous regions consist of a cross-linked polyaniline/polysiloxane network. Thus, the polysiloxane is inducing an antiplasticization effect in polyaniline base as the T_g is increased. Generally, plasticizers reduce T_g. GPC data (Figure 11) is consistent with this model. The addition of the poly-amino containing siloxane to a polyaniline base solution in NMP results in a significant increase in the high molecular weight fractions depicting the cross-linked network which forms between polyaniline and the plasticizer.

In addition to the cross-linked network the siloxane induces in the amorphous regions, concomitantly it also is found to induce significant levels of crystallinity in polyaniline base as a result of the local mobility that it provides. Figure 5c shows the WAXS for a polyaniline base film processed from NMP containing 10% of the poly amino containing siloxane. As can be seen highly crystalline polyaniline has been attained. Much higher levels of crystallinity as compared to figure 5b for the stretch oriented films.

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Thus polyaniline by the addition of the siloxane forms a structure depicted in Figure 6 where crystalline regions of highly associated polyaniline chains (outlined by a rectangle) are formed with interstitial amorphous regions. In most cases, the additive resides in the amorphous interstitial sites. The degree of crystallinity (number of crystalline sites) and the size of the crystalline domains as well as the degree of amorphous regions and the nature of the amorphous region (aggregated, i.e. cross-linked or not) can be tuned by the type and amount of additive. In turn, by controlling the above, the properties of the material can also be controlled.

With the poly -co-dimethyl aminopropyl siloxane (5% N content), loadings ranging from .001 to 20 % by weight gives highly crystalline polyaniline. The highly crystalline polyaniline in turn exhibits increased modulus, stiffness, yield and tensile strengths, hardness, density and softening points. Thus, the siloxane at these loadings is having an antiplasticization effect. Above 20% loading, the crystallinity begins to decrease. As the crystallinity decreases, the modulus, stiffness, yield and tensile strengths, hardness, density and softening points begin to decrease. Thus, the siloxane at these loadings begins to have a plasticization effect. The siloxane content becomes high enough that it disrupts the polyaniline base interactions in the crystalline regions. With the poly co dimethyl aminopropyl siloxanes having .5 and 13% N ratios, similar trends are observed but the particular amount of siloxane needed to have a plasticization effect or an antiplasticization effect varies. Thus, the degree of crystallinity and the degree of amorphous regions and in turn the properties of polyaniline can be tuned by the nature of the additive as well as the amount of additive. Indeed, using the same additive but simply changing the loading dramatically changes the morphology and in turn the properties of polyaniline.

The electronic properties of the polymer are also impacted. The conductivity of a polyaniline base film cast from NMP and containing 1% by weight poly-co-dimethyl aminopropyl siloxane

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which is doped by aqueous hydrochloric acid is 50 S/cm as compared to 1 S/cm for a polyaniline film with no plasticizer. This is isotropic conductivity. The doped film containing the polysiloxane retains the highly crystalline structure.

The degree of crystallinity and the degree of amorphous regions and in turn the physical, mechanical, and electronic properties can be tuned by the particular additive used and by the amount of additive. For example, the Tg of polyaniline can be increased or decreased by the amount and type of additive. The mechanical properties such as tensile properties, modulus, impact resistance, etc. can be tuned as described above. The additive can range from .001 to 90% by weight, more preferably from .001 to 50% and most preferably from .001 to 25%. A list of plasticizers that can be used to practice the present invention is given in Table 1. The plasticizer can be small molecules, oligomeric or polymeric in nature as can be seen in Table 1. They can be monofunctional, bifunctional, and multifunctional. The additive can also be removed from the final film structure if so desired by appropriate extraction.

Specific Examples

Polyaniline Synthesis Polyaniline is synthesized by the oxidative polymerization of aniline using ammonium peroxydisulfate in aqueous hydrochloric acid. The polyaniline hydrochloride precipitates from solution. The polymer is then neutralized using aqueous ammonium hydroxide. The neutralized or non-dope polyaniline base is then filtered, washed and dried. Polyaniline can also be made by electrochemical oxidative polymerization as taught by W. Huang, B. Humphrey, and A.G. MacDiarmid, J. Chem. Soc., Faraday Trans. 1, 82, 2385, 1986.

Polyaniline Base in NMP: The polyaniline base powder is readily dissolved in NMP up to 5% solids. Thin films (on the order of a micron) can be formed by spin-coating. Thick films